

PYROLYTIC AND SPECTROSCOPIC APPROACHES TO THE STUDY OF REFRACTORY FORMS OF ORGANIC CARBON. SOILS AFFECTED BY FIRES.

¹F.J. GONZÁLEZ-VILA, ¹J.A. GONZÁLEZ; ¹O. POLVILLO, ²G. ALMENDROS, ³H. KNICKER

¹Instituto de Recursos Naturales y Agrobiología, CSIC, P.O. Box 1052, 41080 Sevilla,

²Centro de Ciencias Medioambientales, CSIC, Serrano 115 bis, 28006 Madrid, Spain

³Lehrstuhl für Bodenkunde, TU München, 85350 Freising-Weihestephan, Germany

Abstract: Vegetation fires and fuel-wood combustion transfer carbon from the relatively fast biological-atmosphere carbon turnover to the long-term geological one, the processes in which biomass burning is involved, may represent a significant sink for carbon dioxide. The so-called “black coal”, is composed mainly of polyaromatic and relatively inert carbon forms. In this work, the composition of the potential refractory carbon forms present in the different soil particle fractions of a pine forest soils from Sierra de Aznalcollar, Seville, Spain affected and unaffected by a wildfire is described using pyrolytic (Py-CG/MS) and spectroscopic solid state ¹³C NMR techniques. An enrichment in total carbon was found for all particle size fractions in the fire affected soil, with the lowest enrichment factor in the sand-size fraction (1.4) and the highest in the coarse silt-size (2.8) and clay-size fractions (2.7). When analysing the pyrograms of the forest soils affected by fire, most pyrolysis products present in undisturbed natural soils disappears and the dominance of charred “non pyrolyzable” refractory carbonous material is clear. The formation of condensed refractory materials after the wildfire is again apparent in the solid-state ¹³C NMR spectra, showing a neat increase in the intensity of the aromatic C region (160 to 110 ppm), which occurs at the expenses of the O- and N-alkyl C region (110 to 60 ppm). This together with other evidences, indicates that the increase in C observed in all size fractions of the fire affected soil is mainly due to the formation of refractory, polyaromatic and relatively inert carbonaceous (Black coal) material, rather than to the input of fresh litter after the fire event.

Resumen: Los incendios forestales y la combustión de madera transfieren carbono del ciclo relativamente rápido, biota-atmosfera, a uno, mucho más largo, geológico, en el que la biomasa quemada puede representar un sumidero significativo para el dióxido de carbono. El “carbón negro o carbón vegetal” está compuesto fundamentalmente por formas de carbono poliaromáticas inertes. En este trabajo se estudian mediante técnicas de pirólisis (Py-CG/MS) y espectroscopía de resonancia magnética nuclear (¹³C NMR) la composición de las formas de Carbono refractarias presentes en las diferentes partículas de suelos forestales con pinar de la Sierra de Aznalcóllar, Sevilla (España) afectados y no afectados por incendios. Se ha observado un enriquecimiento en Carbono total para todos los tamaños de partícula en los suelos afectados por el fuego, con el menor factor de enriquecimiento en la fracción arena (1.4) y los mayores en las fracciones limo grueso (2.8) y arcilla (2.7). En los pirogramas de suelos forestales afectados por el fuego no se identifican la mayoría de los compuestos producidos en la pirólisis de los suelos no afectados y, en cambio, hay un predominio de materiales orgánicos refractarios no pirolizables. La formación de materiales refractarios condensados después del incendio es identificada también en los espectros de ¹³C RMN que presentan un claro incremento en la intensidad de la región de los C aromáticos (160 a 110 ppm), producida a expensas de la región de los grupos O y N alquílicos (110-60 ppm). Esto, unido al resto de las evidencias indica que el incremento de C observado en todas las fracciones de los suelos afectados por el fuego se debe principalmente a la formación de compuestos orgánicos poliaromáticos refractarios (black coal) más que a los nuevos aportes de materia orgánica fresca producidos tras el evento de incendio.

Palabras clave: Tamaño de partícula, Secuestro de Carbono, Carbono refractario, Py-GC/MS, ¹³C RMN

Key words: soil size fractions, carbon sequestration, refractory carbon, Py-GC/MS, NMR

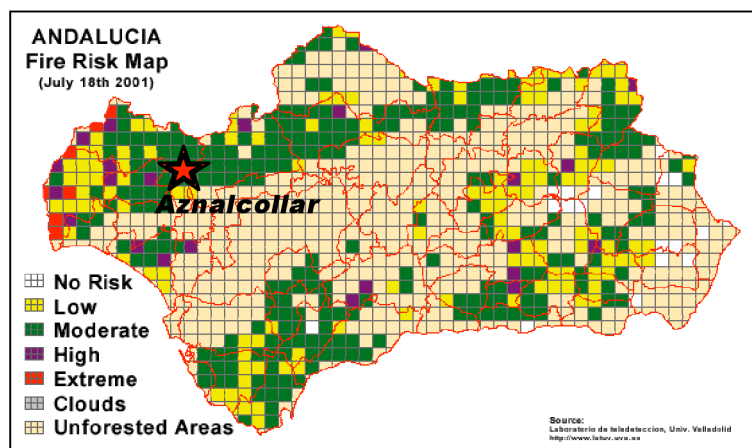


FIGURE 1. Andalusia Autonomous Community fire risk map with the location of the study area at “Sierra de Aznalcollar”, Seville. (Fire risk map from Laboratorio de Teledetección, Universidad de Valladolid).

RESULTS

The concentration of C associated with each fraction of the bulk soil is shown in Table 1. Taking the fire unaffected soil (FU) as a reference, the carbon enrichment factor (EF) was also calculated for each fraction. Although at

different magnitude, all fractions showed an enrichment in carbon. The lowest EF was found in the sand-size fraction (1.4) and the highest in the coarse silt-size (2.8) and clay-size fractions (2.7).

TABLE 1. Yield and carbon distribution in the different soil particle size fractions

Fraction	Yield (% bulk soil)		C (mg g ⁻¹ bulk soil)		
	FU Soil ⁽¹⁾	FA Soil ⁽²⁾	FU Soil	FA Soil	EF ⁽³⁾
Sand (2mm-63µm)	37	39	19	27	1.4
Coarse silt (63-20µm)	9	12	65	181	2.8
Medium silt (20-6µm)	16	17	44	135	3.1
Fine silt (6-2µm)	20	14	5	11	2.1
Clay (<2µm)	19	17	5	13	2.7

(1) Fire unaffected soil; (2) Fire affected soil; (3) Enrichment factor

The pyrograms obtained from the original, fire unaffected soils release a wide variety of typical organic soil pyrolysis compounds (identity not shown here) arising mainly from polysaccharide and polyphenol precursors. On the contrary, in the forest soils affected by fire, most pyrolysis products present in undisturbed natural soils vanishes and the dominance of charred “non pyrolyzable” refractory carbon

material is clear (Figure 2).

The pyrograms obtained from the original, fire unaffected soils release a wide variety of typical organic soil pyrolysis compounds (identity not shown here) arising mainly from polysaccharide and polyphenol precursors. On the contrary, in the forest soils affected by fire, most pyrolysis products present in undisturbed natural soils vanishes and the dominance of

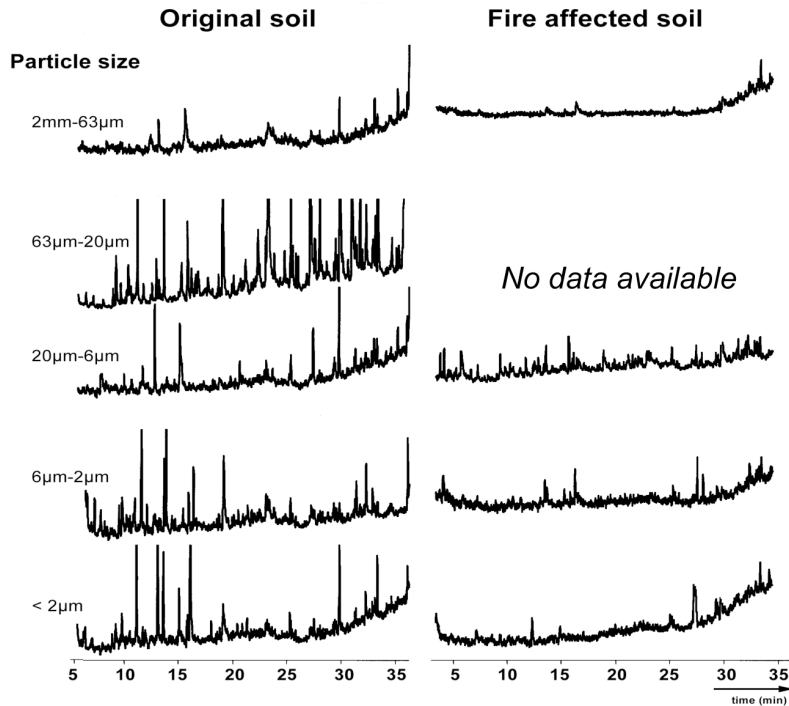


FIGURE 2. Changes in pyrograms patterns of the particle size fractions from raw soil samples from a pine forest at Sierra de Aznalcollar, unaffected and affected by a severe forest fire

charred “non pyrolyzable” refractory carbonous material is clear (Figure 2).

The formation of condensed refractory materials after a forest fire is again apparent in the solid-state ^{13}C NMR spectra from the same samples. In general, a neat increase in the intensity of the aromatic C region (160 to 110 ppm) is observed, dominance which occurs at the expenses of the O- and N- alkyl C region (110 to 60 ppm), that decreases in all particle size fractions of the fire affected soil (Fig. 3). This indicates that the increase in C observed (enrichment factor) in the fire affected soil is mainly due to the enrichment of soil in charred material rather than due to the input of fresh lit-

ter after the fire event, and that charred material became associated to all particle size fractions. This is further corroborated when analysing the RNM Ratio I (160/110 ppm)/(110/45 ppm), that is < 1 in all particle fractions of the original, unaffected soil and > 1 in all particle fractions of the fire affected one.

Another indicator of organic matter condensation and the formation of refractory, polyaromatic and relatively inert carbon forms (Black coal), is that the O-alkyl C/alkyl C ratio, also decrease in the fire affected soil associated to particle size, this ratio is always lower than that in the original non fire affected soil.

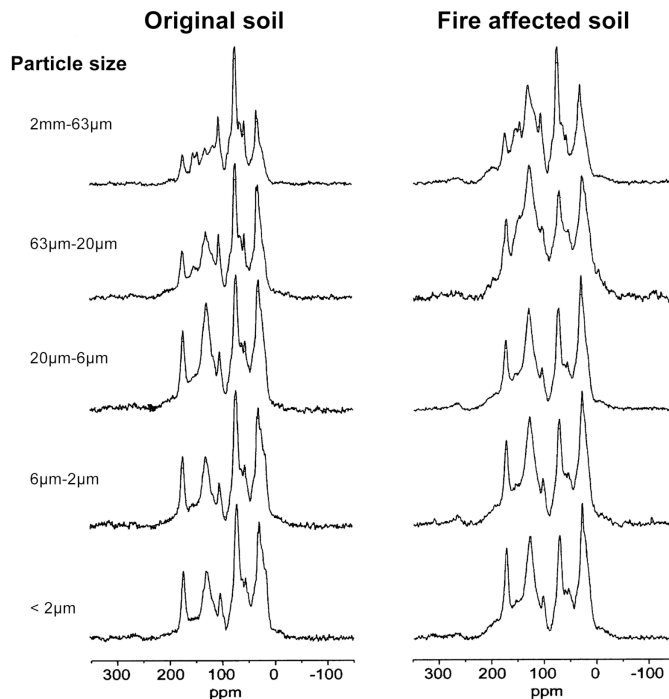


FIGURE 3. Changes on the solid-state ^{13}C NMR spectra of the particle size fractions from soil samples from a pine forest at Sierra de Aznalcollar, unaffected and affected by a severe forest fire

REFERENCES

- Almendros, G., González-Vila, F.J., Martín, F. (1990). Fire-induced transformation of soil organic matter from an oak forest: an experimental approach to the effects of fire on humic substances. *Soil Science* 149, 158-168.
- Goldberg, E.D. (1985). Black Carbon in the Environment: Properties and Distribution. *Wiley Interscience*, New York.
- González-Vila, F.J., Tinoco, P., Almendros, G., Martín, F. (2001). Pyrolysis-GC-MS Analysis of the Formation and Degradation Stages of Charred Residues from Lignocellulosic Biomass. *Journal of Agricultural and Food Chemistry* 49, 1128-1131.
- Haumaier, L. y Zech, W. (1995). Black carbon-possible source of highly aromatic components of soil humic acids. *Organic geochemistry* 23, 191-196.
- Schmidt, M.W.I., Skjemstad, J.O. y Kogel-Knabner, I. (1999). Charred organic carbon in German chernozemic soils. *European Journal of Soil Science* 50, 351-365